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Water Ice and Life's Roots in Space

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Nearly three decades ago as Voyager 2 spacecraft raced out of the Solar System. NASA engineers turned its camera arm around (at the request of the American astronomer Carl Sagan) to take a parting snapshot of Earth. Earth's image was a single pale blue pixel, its color caused by the Rayleigh scattering of sunlight in the water of our oceans. Earth is a water planet, and this is the color of life. No matter how far we travel on our planet, no matter how high or deep, if we find liquid water, we find some form of life that manages to survive there.

And yet there is a cruel irony. Water in its solid crystalline form is hostile to life. Organisms can roost in geysers, wallow in brine and gulp down acid, but they cower from ice. The rigid ordering of water molecules in ice crystals expels impurities and tears organic tissue beyond repair. In fact, about the only good thing you can say about ice is that it gets out of the way: Its low density ensures that it floats and leaves the water-dwelling creatures in peace.

Recent discoveries have caused us to rethink this basic premise. New lines of evidence – both observational and experimental – suggest that prebiotic organic compounds are not only comfortable in, but in fact *had their origin in* a peculiar form of solid water ice that is ubiquitous in interstellar space, but completely absent from Earth.

Only recently have we been able to create even submicroscopic quantities of this ice in terrestrial laboratories, yet it constitutes the most abundant form of water in the universe. Interstellar ice is a far cry from the ice we are so familiar with on Earth. This interstellar ice has no crystalline structure, and despite the fact that its temperature is a scant few degrees above absolute zero (where all molecular motion ceases), it is highly reactive and can flow like water when exposed to radiation. It is in fact this ice's similarity to liquid water that allows it to participate in the creation of the very first organic compounds.

By way of comets, interstellar ice and the organic compounds that formed within it may have seeded the Earth with the starting materials for the origin of life. The natural history of water ice from its origin as frost on interstellar grains to its ultimate disposition as liquid water in habitable zones such as exist on our Earth is still a matter of vigorous research (and debate). Water – the principal component of life and the substance that covers nearly 3/4 of our planet's surface, still has secrets to reveal.

Water ice as a material

To understand the many roles that water ice plays in the synthesis of organic compounds and their ultimate delivery to the Earth, we first need to look at some peculiarities of its structure. It is, after all the structure of water ice – how the molecules are joined together one to another - that dictates all other properties of the material. A water molecule consists of an oxygen atom having two slightly negatively charged, paired electrons and two slightly positively charged, chemically bound hydrogen atoms. When water molecules come together, the paired electrons of one water molecule form weak bonds with the hydrogen atoms of an adjacent water molecule. This association is called a “hydrogen bond” and is the principal reason for the remarkable properties of water. As a result, each oxygen atom is held by four bonds in a tetrahedral framework. When such a framework is neatly organized over many hundreds of molecules, it is called a crystalline material.

There are many ways to regularly stack the oxygen atoms in three dimensions, each leading to a different crystalline phase of water ice. Most are stable only under high pressure. Indeed, experiments conducted at elevated pressure have revealed at least 12 different crystalline phases of water ice, usually designated as Ice I – Ice XII. Nature is usually only concerned with the low-pressure form of water ice, Ice I, in which the stacking of the network of oxygens forms a hexagonal pattern as manifested in the shape of snowflakes. At lowered temperature, the oxygens can also stack in a cubic pattern, or even be prevented from forming any long-range order at all. All of these arrangements leave fairly large open spaces between the oxygen atoms, called interstitial sites.

It may be surprising to learn that water in its liquid state maintains much of the bonding network that is characteristic of crystalline ice. The essential difference – and this is a critical one for life – is that in liquid water the hydrogen bonds are rapidly redistributed and the oxygen atoms are free to move into the large interstitial sites of the structure. At the molecular level, liquid water is able to adjust its structure to accommodate the physical and chemical requirements of living things.

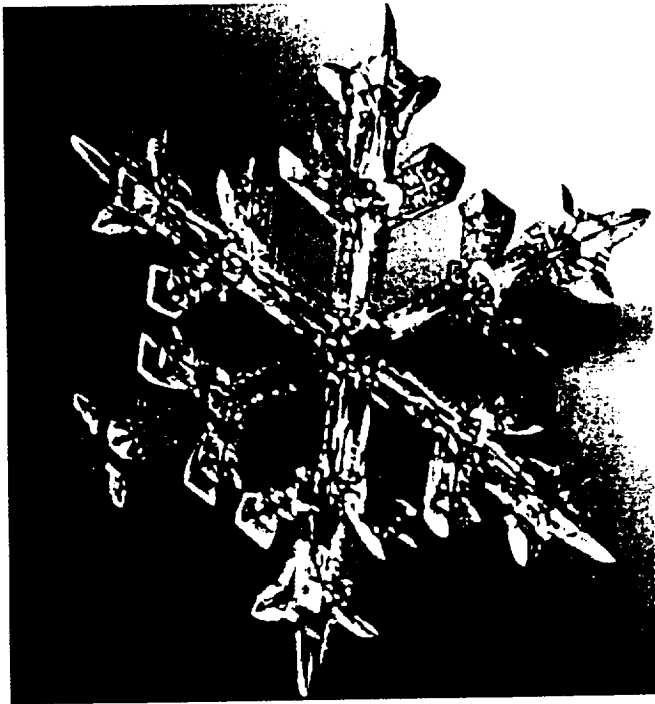


Figure 1. Snow flake, courtesy of Kenneth G. Libbrecht, Caltech University.

Water and ice in the habitable zone

We owe our existence to the fact that our planet is in a “habitable zone” near a star where water can exist naturally in a liquid state, a necessity for life as we know it. This requirement dictates a fairly narrow temperature regime, between 273 – 373 Kelvin or 0 – 100° centigrade, (a slightly wider margin if one allows for salinity or high pressure). On Earth, pure water ice exists naturally in only one crystalline phase, hexagonal ice,

whose symmetry is exhibited in the myriad shapes of snowflakes. Outside of the habitable zone, water is generally thought to be in a solid or gaseous form.

Ice in our universe – and in the laboratory

The water and ice of our Earth are definitely in the minority when we consider the cosmos. Most ice in the universe is condensed as a thin frost on sub-micron ($<10^{-6}$ meters, about 1/100 the diameter of a human hair) interstellar dust grains. This ice was created under very cold conditions and very slowly by the recombination of oxygen and hydrogen atoms. Water may also have directly condensed from the gas phase onto the very cold dust grains. Temperatures are only about ten degrees of absolute zero and molecules present themselves at a typical rate of one atom per day. The resulting water ice structure is highly disordered. Unlike crystalline ice, this amorphous ice can trap impurity molecules such as carbon monoxide (CO) and ammonia (NH₃), setting the stage for the formation of the first organic compounds.

All of the observed properties of water ice are a function of the arrangement of the water molecules in the solid, which can be studied directly by structure-sensitive techniques such as diffraction. In our laboratory at NASA Ames Research Center, the low-pressure forms of water ice are studied by means of electron diffraction. We make films of water ice only a few hundred molecules thick by freezing water vapor inside a specially modified cryogenic Transmission Electron Microscope (TEM). High-magnification images and electron diffraction patterns are recorded as the ice films are warmed or annealed to study changes in morphology and structure as they occur in real time.

Fig. 2. Picture of David and Peter creating conditions in the TEM known to exist in the cores of interstellar molecular gas and dust clouds.

When the temperature is low enough, < 30 K or -243° C, and molecules are deposited slowly enough (less than a few microns per hour), an amorphous solid results that should be very similar to interstellar ice. This ice has no long-range molecular or atomic order, no crystalline surfaces, and would appear as transparent as window glass to an interstellar traveler. Despite the fact that only submicroscopic quantities of this ice have been created in our laboratories on the Earth, it is the most abundant form of ice in the universe.

In 1993 we first recorded electron diffraction patterns from ice made in this way. To our surprise, the patterns could be best explained if interstitial oxygen atoms occupied positions midway between the locations of the first and second oxygen-oxygen distances in normal water ice. This overpacking of oxygen atoms yields a density of 1.1 g/cc for the solid structure, vs. 0.94 g/cc for ordinary ice. This is why the ice is called "high-density amorphous ice" or in short-hand notation, Ia_h . This high-density amorphous form of water ice was first reported from X-ray diffraction experiments by the American chemist Narten in 1976, but was later (incorrectly, it turns out) considered to be an artifact of the experiment.

All forms of water ice when cooled below a few tens of degrees Kelvin should persist nearly indefinitely – there is simply too little thermal energy available to break the hydrogen bonds that hold the structures together. However we found that no water ice other than Ia_h will survive at temperatures lower than 30 K when exposed for more than a brief instant to the high-energy electrons of our TEM. All other forms of water ice when irradiated in this way transform to high-density amorphous ice. Given a bit of practice, we found that we could even write our names in Ia_h by judicious movement of the microscope controls.

The German physicist Heide first reported this property of Ia_h 1984. Heide also discovered that when energy is deposited in the ice by electrons, photons or heavy particles, the ice restructures much like liquid water - that is, it flows! We now understand that overpacked oxygen atoms in the high-density amorphous ice and the defects that exist as a result of their bonding make molecular mobility within the structure much easier. Ia_h is a form of solid amorphous water that takes on the viscosity of a liquid when exposed to very localized energy discharges. When Ia_h containing impurities such as CO and NH_3 is exposed to energetic particles or photons, radicals are formed which can migrate within the ice until they chemically combine with other reactive species. This unique property explains the origin of the first organic compounds in water-rich interstellar ices.

The chemical evolution of irradiated ices in the cores of interstellar clouds has been extensively studied following the pioneering work of Mayo Greenberg of Leiden University and Lou Allamandola of NASA/Ames Research Center. It has been shown for example that organic molecules such as CH_3OH and even CH_3CH_2CN are created in interstellar ice. Indeed, over 100 organic compounds have been detected in cold molecular clouds, many of which are thought to be formed on or in interstellar ice grains.

Fig. 3a Structure model, Diffraction Pattern, Radial Dist. Function and Image of Ia_h

Fig. 3b Structure model, Diffraction Pattern, Radial Dist. Function and image of Ia_i

Fig. 3c Structure model, Diffraction Pattern, Radial Dist Function of Ic

Fig. 3d Structure model, Diffraction Pattern, Radial Dist Function and image of Ih

The formation of icy planetesimals

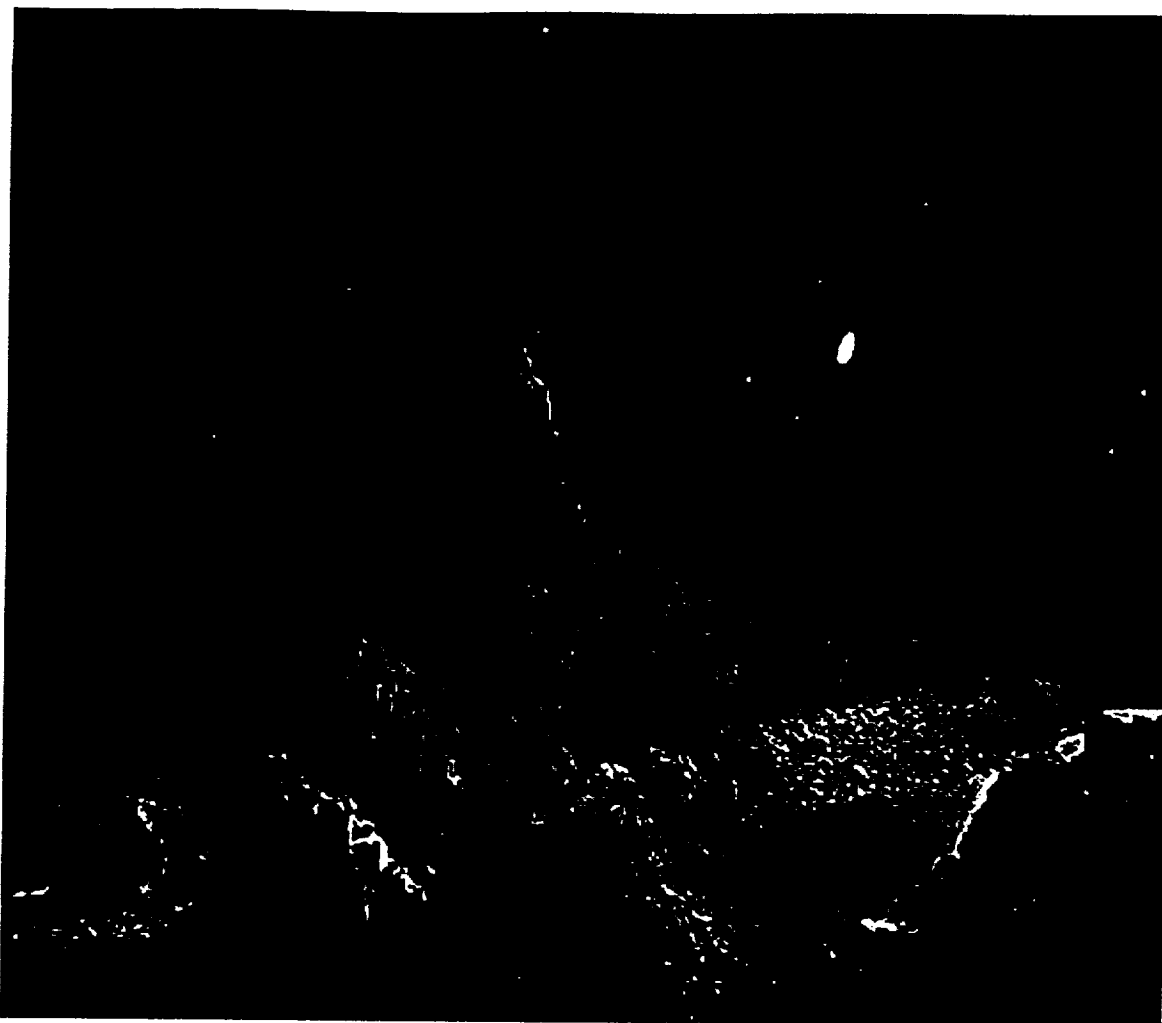
Other interesting forms of water ice are encountered when interstellar dust grains coalesce in the gravitational collapse of cold molecular clouds during star formation. When our solar system was forming, temperatures near the protosun were high enough to volatilize all but the most refractory elements and compounds. However, in cooler

regions of the solar nebula outside the orbit of Jupiter, conditions existed which may have allowed pristine interstellar grains to coalesce into 1-500 km diameter icy planetesimals.

In the agglomeration process, the water ice was warmed to some extent. How much warming was experienced by the grains is a matter of debate, but the observed volatile content of comets (which are relicts of icy planetesimals) suggests that the increase could have been as much as 50 K. A heating event of this magnitude is sufficient to change the structure of the original Ia_h to another amorphous form of water ice called low-density amorphous ice (Ia_l). During this structural change, hydrogen bonds break and reform, allowing for the movement and chemical recombination of radicals within the ice. This transition, which in our experiments occurs between 35-65 K, marks another opportunity for organic synthesis within impure water ice, driven by the softening of the ice matrix and the availability of reactive hydrogen and small carbon- and nitrogen-containing molecules.

Ia_l can also be formed directly by the slow condensation of water from the vapor phase at temperatures between 65 – 120 K, and even by rapid freezing of liquid water droplets. This form of water ice is of great interest in biological electron microscopy, because it helps preserve cell structure in the freezing process. Ia_l has the open structure of (and the same density as) crystalline hexagonal water ice, but retains sufficient disorder to be an amorphous solid. Ia_l efficiently holds or traps impurities that are released only at higher temperatures.

Most water ice in comets must be in this low-density amorphous form, because the abundance of volatiles in comet gas tails implies that the ice is very efficient in trapping such molecules. For example, comets typically release CO and CH₄ at much higher temperatures than would be expected if these highly volatile molecules were frozen as pure discrete phases. The vaporization of these molecules at anomalously high temperatures suggests that changes in the water ice structure (in which these molecules are trapped) control their release.



*Figure 4 - Image of comet Hale-Bopp Francesca Lucentini and Marco Paolo Pavese.
From Monfrague, Italy, on April 19, 1997 21:00 PM. Contact: mpp@ed.it (Marco)*

The water ice in comets

Ia_1 exhibits an interesting property as it is warmed – it experiences what is called a *glass transition* at temperatures of 125-135 K. During the glass transition, a thermodynamic change of state occurs in which a material that is essentially a glassy solid becomes a viscous liquid. The nature of this transition in water ice, which marks a change in its physical and thermodynamic properties, has long been a matter of debate. Is the change in viscosity due to molecular diffusion (bulk movement of water molecules), or some other physical process? In 1997, in a remarkable set of experiments Steve Fisher and J. Paul Devlin of Oklahoma State University demonstrated the true nature of the glass

transition in water ice. Oxygen atoms in the structure remain fixed in place while hydrogen bonds break and reform through a series of choreographed steps involving the motion of defects (protons or holes) through the structure. This discovery sheds light on the chemical reactivity of amorphous water ice as it is heated through the glass transition temperature. Like the $Ia_h \rightarrow Ia_i$ transition, the glass transition involves the making and breaking of hydrogen bonds, providing yet another opportunity for radical recombination and organic synthesis in the water ice matrix.

Thus, at high enough temperature (but still a chilly -150°C), amorphous water ice turns into a viscous liquid. This unusual viscous liquid water, which we first encountered in 1994 and which we call restrained amorphous ice, Ia_r , was never thought to be of interest in nature. Most ice specialists believed that only 10 K above the glass transition temperature Ia_r crystallizes into the cubic crystalline form Ic . However, when studying the time course of $Ia_r \rightarrow Ic$ crystallization in the electron microscope, we found that there always remains a distinct amorphous component in the diffraction patterns in the cubic temperature regime (150 - 200 K). Only about a third of the ice ever crystallizes – the balance remains in the disordered Ia_r form.

The structure of Ia_r has not yet been resolved. However, some insight can be gained into its nature by slow crystallization experiments in which the ice is kept at the minimum crystallization temperature for long periods of time. As crystallization proceeds, diffraction patterns exhibit peaks that arise from both hexagonal and cubic structures within the ice. In TEM images, the crystals formed are seen to contain a myriad of defects – stacking faults which represent the boundaries between domains of cubic and hexagonal packing. From this, we infer that incipient local ordering occurs at the glass transition temperature, yielding unit cell domains of hexagonal and cubic order. These domains increase in size until a highly faulted structure results.

Most of the ice, however, remains in submicroscopic cubic domain, because the cubic stacking of oxygens is kinetically favored. Another structural clue comes from studies of water ice nanoclusters, which are clusters of water molecules 10-100 nm in diameter.

These nanoclusters were first made by Lance Delzeit and J. Paul Devlin at Oklahoma State University to study the surface chemistry of ice. In 1998, we found in collaboration with Lance Delzeit who was a Post-doctoral fellow at Ames, that even though the interior of these grains is cubic crystalline ice, the surface and near-surface layers are in fact amorphous and highly reactive. Thus, several layers of water between cubic domains apparently retain the chemical reactivity of amorphous ice.

Restrained amorphous water ice above the glass transition is a different form of liquid water than we are familiar with. Unlike the liquid water of our oceans, this viscous liquid resists crystallization. The crystallization of Ia_h proceeds gradually, characterized by only one activation energy barrier that is equivalent to the energy needed to break two hydrogen bonds per molecule, on average. As physicist C.A. Angel of Arizona State University pointed out, this behavior is typical of "strong" glassy liquids, such as molten silica above its glass transition temperature. On the other hand, the liquid water we are familiar with on Earth has a range of activation energy barriers that result in low viscosity.

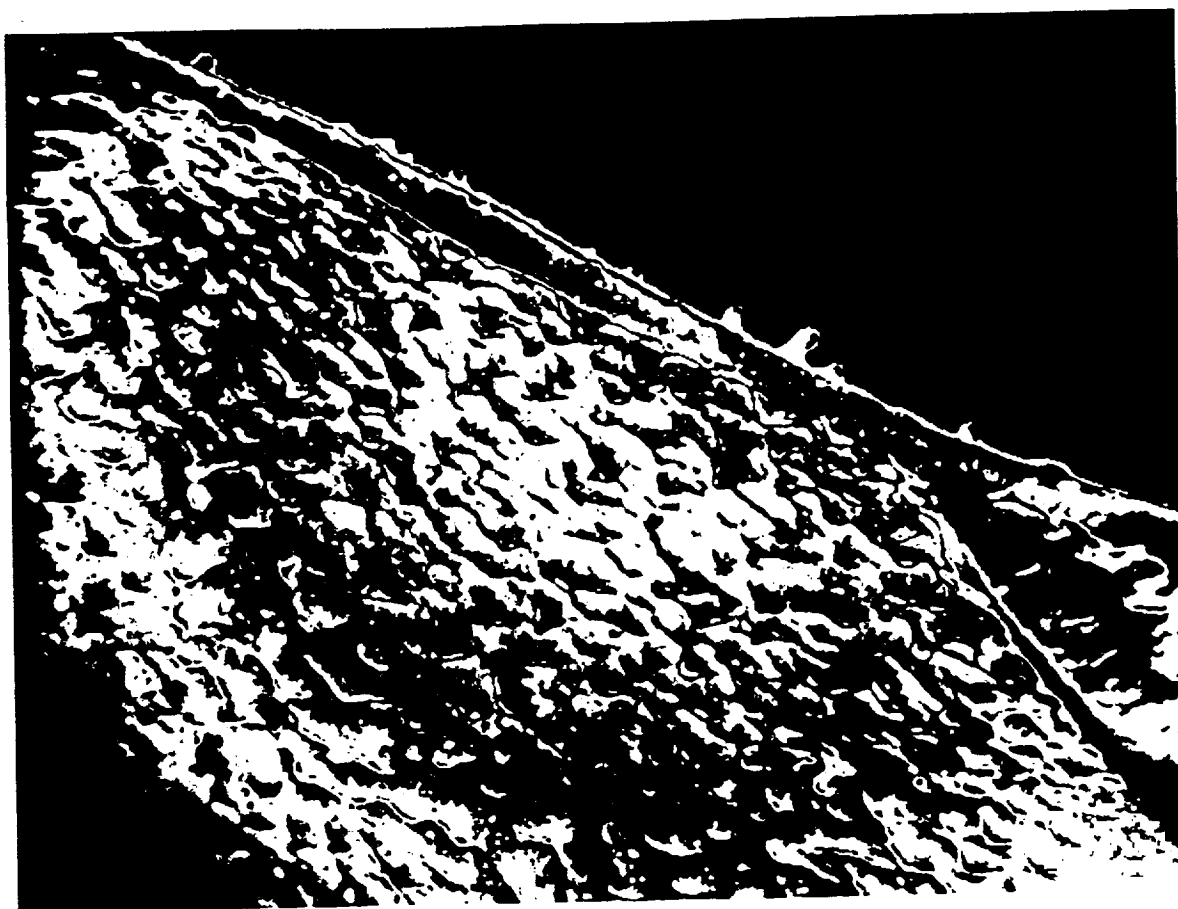


Fig. 5 - Image of "melted" I_a ice layer.

Ice in the habitable zone.

And that brings us, finally, back to the more familiar form of water ice on Earth. Further warming of the cubic ice and strong liquid water (I_a) mixture until about 200 K (still a bone-chilling -73°C) will lead to complete restructuring of the ice into its stable hexagonal form (I_h). During this recrystallization, all remaining volatiles are excluded from the solid. From this point on, water ice at low-pressure is much as we know it: snow flakes, glaciers, the ice cubes in our drinks. Crystalline hexagonal water ice, the only stable form of water ice at low pressure, will persist until melting or vaporization takes place.

Just last year, Astrochemist Lou Allamandola and colleagues at NASA Ames Research Center, and Chemist Dave Deamer of the University of California, Santa Cruz, found that when impure, energetically processed interstellar ice analogs are melted, the organic compounds within the ice form spherical vesicles reminiscent of primitive cellular membranes. This is a huge step closer to the origin of simple life, since all life as we know it requires an envelope of some kind to act as a potential energy barrier and to concentrate the molecules necessary for metabolism and replication.

Thus, water was present at every step in the creation of the molecules required for the origin of life. Not only liquid water, but also exotic forms of water ice with physical properties similar to the liquid, that we only now gradually learn to understand.